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(54) POLYESTER COMPOSITION

(71) We, "FOKKER-VFW" N.V. a company registered under the Laws of The Netherlands, of Schiphol-Oost, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to fire-retardant polyester moulding compositions and to articles made therefrom.

Polyester moulding compositions generally comprise a mixture of an unsaturated polyester with an unsaturated monomer copolymerisable therewith, to which may have been added a polymerisation catalyst, an accelerator and occasionally fillers, reinforcement fibres, colorants and other convential additives. The combustability of such compositions, and of the articles made therefrom, is frequently reduced by adding chlorinated paraffins and/or aromatic phosphoric acid esters thereto. For the same purpose, chlorine may be chemically incorporated in the unsaturated polyester component before forming the composition.

Adding such additives to moulding compositions has meant that the articles made from the moulded and cured compositions are more or less self-extinguishing or flame-resistant when exposed to fire. Nevertheless, and in view of the great variety of uses for such articles, there is a constant need for polyester moulding compositions and polyester resin articles having improved fire-retardant characteristics.

It has now been found that polyester resin articles may be rendered fire-retardant to a high degree by incorporating in their moulding compositions a combination of three materials: a source of carbon, a source of phosphoric acid and a source of non-inflammable gases. When the articles made from such compositions are exposed to high temperatures or even to an open fire, they will superficially give rise to the production of bubbles and foam, thus resulting in a multicellular foam layer at their surface, and such a foam layer will isolate the underlying parts of the article from combustion.

In accordance with the invention, therefore, there is provided a polyester moulding composition comprising an unsaturated polyester, an unsaturated monomer copolymerisable therewith, a phosphate material which yields phosphoric acid on thermal decomposition, a carbon-containing material containing radicals which enter into an esterification reaction with phosphoric acid, having a decomposition temperature above that of the phosphate material, and which when heated with the phosphate material, produces carbon, and a material which yields a non-inflamable gas when heated.

In a further aspect of the invention, there is provided fire-retardant shaped articles consisting partially or completely of a resin material formed by curing a polyester composition according to the invention.

A combination of the three aforesaid materials has previously been used in paints (and are known as intumescent coatings), but their use in polyester moulding compositions and consequently their use throughout the mass of a polyester resin has never previously been proposed.

In the moulding compositions of the in-

vention, any combination of unsaturated polyester and unsaturated copolymerisable monomer may be used. Furthermore, any commercial type of polymerisation catalyst, accelerator, fillers, reinforcement fibers, or other additives may be added if desired. The presence of a proportion of chlorine in the polyester component, for instance if this component comprises hexachloro endomethylene-tetrahydrophtalic acid (HET-acid or chloroendic acid), is not objectionable and may even be advantageous.

The carbon-containing material used in the invention is generally a material containing radicals capable of entering into an esterification reaction with phosphoric acid. The material has a high carbon content and decomposes at a higher temperature than the phosphate material. Typical examples of carbon-containing materials are starch, casein, and polyhydric alcohols such as pentaerytritol. Mono-, di- and tripenta-erytritol and mixtures thereof are preferred.

The phosphate material may be any material which decomposes at a lower temperature than the carbon-containing material thereby generating phosphoric acid. Typical examples are ammonium orthophosphate and polyphosphoryl phosphate. The preferred phosphate material is a commercially-available nitrogen-containing polymer phosphate which comprises more phosphoric acid than other similar materials and which is moreover water-insoluble.

The material which yields a non-inflammable gas is generally a mixture of two substances having different decomposition temperatures (for identification purposes these two substances will be termed as having "high" and "low" decomposition temperatures, respectively). The substance of low decomposition temperature is preferably an amine or amide, such as dicyanodiamide, urea, melamine, or guanidine, and the substance of high decomposition temperature is preferably a chlorinated hydrocarbon such as chlorinated naphthalene. The substance of high decomposition temperature may be omitted partially or completely from the moulding composition if chlorine is incorporated chemically in the polyester component.

The concentrations of the various materials in the polyester moulding compositions, as well as their mutual ratios are not critical. The time and sequence of adding these materials to the other components of the composition is not essential, although it is preferred to incorporate the carbon-containing material, the phosphate material and the material which yields a non-inflammable gas prior to admixing the catalyst and accelerator thereto. In special cases, such as cold-setting polyester resins where the catalyst is active at room temperature, a non-catalysed composition may be initially formed for storage and shipping, and the required catalyst may be added at a later stage just prior to moulding.

After the polyester molding composition has been formed, it may be introduced into a mould and be moulded and cured therein in a conventional way to form massive or hollow articles. The fire-retardant additives are then integrated completely in the mass of polyester resin constituting such articles.

As an alternative to the moulding technique, the moulding composition may be laminated with one or more layers of glass fiber reinforcement and cured to form a fire-retardant laminate.

Another possibility is to form sandwiches having a core of foam plastics or honeycomb material or another suitable core material and skin sheets of fire-retardant glass-fiber-reinforced polyester resin formed from a polyester moulding composition according to the invention. In that case, it will be advantageous to impregnate glass fibers with the moulding composition in which the catalyst is only operative at elevated temperatures, then to apply the resulting sheets of impregnated glass fibers to a core material and thereafter introducing the whole combination into a mould for curing by means of heat and pressure.

The shaped articles produced from polyester moulding compositions according to the invention are suitably protected against fire and other forms of excessive heating owing to the combination of the three materials incorporated therein. Although the invention is not to be restricted by any theoretical explanation of the fire-retardant effect, it is assumed that the phosphate material decomposes first during excessive heating and liberates phosphoric acid, which reacts immediately with the carbon-containing material to form a rather complex ester. The ester then decomposes to form a large volume of carbon, additional water, carbon dioxide and other non-inflammable gas. Phosphoric acid is recovered and this may commence further esterification with the carbon-containing material. Simultaneously with the ester decomposition, the material which yields a non-inflammable gas decomposes and liberates a large volume of non-inflammable gas. The result is a bubbling and boiling mass which develops multicellular foam forming a thick isolating layer and protecting the underlying portions of the article against further attack.

The invention is of great advantage for polyester resin articles required to satisfy high standards of security, e.g. aircraft parts, automobile parts, housing walls and plant walls.

The following Examples of the invention are given by way of illustration.

Example 1

A mixture was prepared from 415 grams of unsaturated chlorendic-acid-based polyester (Hetron 92, from Hooker Chemical; a polyester formed from chlorendic anhydride, maleic anhydride, and ethylene glycol), 55 grams of styrene, 90 grams of toluene, 13 grams of talcum powder (thixotropic agent), 52 grams of dipentaerytritol, 288 grams of Phos-Chek P 30 (a nitrogen-containing polymer phosphate, from Monsanto), 74 grams of melamines and 13 grams of Chlorowax 70 or Cerechlor 70 (Trade Marks for chlorinated naphthalene). The resulting non-catalysed polyester composition (100 grams) was a viscous opalescent product having an acid number of no more than 32 and was stable for at least six months at room temperature (20°C).

The composition was completed for moulding by mixing 100 parts of it by weight with 4 parts by weight of methyl ethyl ketone peroxide catalyst (50%) and with no more than 2 parts by weight of cobalt octoate accelerator (1% cobalt in styrene).

In a first experiment, the catalyst and accelerator were added in combination to the whole composition and this resulted in a moulding composition having a pot life of 20 to 30 minutes at room temperature (for no more than 500 grams of composition). In another experiment, the catalyst and accelerator were each added to 50 parts by weight of the aforesaid composition and the two parts were then combined afterwards. In the latter case, the resulting composition had a pot life of 8 hours at room temperature (for 100 kilograms).

The moulding compositions of both experiments were laminated with one or more layers of glass fiber reinforcement in such a way that the resulting laminates had a resin layer of no more than 400 g/m^2 at one side, and thereupon the laminates were left to cure. After 4 hours at room temperature, the polyester resin layer was free of tackiness in both cases although the curing operation lasted for at least 2 x 24 hours.

One side of each of the resulting laminates was exposed to an open fire or to heat radiation sources having temperatures up to 1400C, and they spontaneously formed a non-inflammable foam layer which isolated the remainder of each laminate against decomposition and combustion. Each foaming surface was uniform and closed and the foam mass was homogeneous.

Example 2

A non-catalysed polyester composition was prepared in a manner as described in Example 1.

1-3% by weight of benzoyl-peroxide catalyst was then added to the composition and the resulting mixture was applied to a glass fiber mat (30% or more by weight of the composition). The mat was then impregnated with the mixture by rolling. The impregnated mat was stored as a semi-finished article and was afterwards converted to a finished article such as a sandwich by applying it in the form of skin sheets to a core material, introducing the combination into a mould, and curing it by heat and pressure. The resulting finished article had the same fire retardant characteristics as the laminate described in Example 1.

WHAT WE CLAIM IS:

1. A polyester moulding composition comprising an unsaturated polyester, an unsaturated monomer copolymerisable therewith, a phosphate material which yields phosphoric acid on thermal decomposition, a carbon-containing material containing radicals which enter into an esterification reaction with phosphoric acid, having a decomposition temperature above that of the phosphate material, and which, when heated with the phosphate material, produces carbon, and a material which yields a non-inflammable gas when heated.

2. A composition according to claim 1, wherein the carbon-containing material is starch, casein or a polyhydric alcohol.

3. A composition according to claim 2, wherein the carbon-containing material is mono-, di- or pentaerythritol or a mixture of at least two thereof.

4. A composition according to any of claims 1 to 3, wherein the phosphate material is ammonium orthophosphate, melamine phosphate, polyphosphoryl phosphate, or a water-insoluble nitrogen-containing polymer phosphate.

5. A composition according to any of claims 1 to 4, wherein the material which yields a non-inflammable gas comprises two substances having different decomposition temperatures.

6. A composition according to claim 5, wherein the substance of low decomposition temperature is an amine or amide.

7. A composition according to claim 6, wherein the substance of low decomposition temperature is dicyanodiamide, urea, melamine or guanidine.

8. A composition according to claim 5, wherein the substance of high decomposition temperature is a chlorinated hydrocarbon.

9. A composition according to claim 8 wherein the chlorinated hydrocarbon is chlorinated naphthalene.

10. A polyester composition substantially as herein described in either of the Examples.

11. Articles consisting partially or completely of a resin material formed by curing

a polyester composition according to any of claims 1 to 10.

12. A laminate comprising one or more layers of glass fiber reinforcement and one or more layers of a resin composition formed by curing a polyester composition according to any of claims 1 to 10.

13. A sheet of glass fibers impregnated with a polyester composition according to any of claims 1 to 10.

14. A laminate comprising a core and skin sheets adhering thereto comprising impregnated glass fiber sheets according to claim 13 in which the polyester composition is cured.

15. Articles according to claim 12 substantially as herein described in either of the Examples.

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